Resonant inelastic soft-x-ray scattering study of heavy-fermion systems

S. M. Butorin,[1] M. Magnuson,[1] K. Ivanov,[2] D. K. Shuh,[2] T. Takahashi,[3] S. Kunii,[3] J.-H. Guo[1] and J. Nordgren[1]

[1]Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

[2]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

[3]Department of Physics, Tohoku University, Sendai 980-77, Japan

INTRODUCTION

As previously demonstrated [1], resonant inelastic x-ray scattering spectroscopy at some core thresholds is an efficient tool for probing both intra-atomic neutral and inter-atomic charge-transfer excitations in rare-earth compounds. As a result of creation-annihilation of a core hole there are radiative transition back to the ground and low-lying excited states so that the final states of the spectroscopic process can be described as eigenvalues of the ground state Hamiltonian. For correlated systems with significant configurational mixing in the ground state, resonant x-ray scattering spectra can be interpreted within the framework of a localized, many-body approach based on a single-impurity Anderson model (SIAM). The ground state values of the charge-transfer energy and hybridization strength which are used as model parameters to characterize charge-transfer excitations can be estimated with higher accuracy from analysis of these data.

The SIAM is very often used for the description of various transport and spectroscopic properties of Ce- and Yb-based systems with the pronounced heavy fermion behavior [2]. The model predicts a significant temperature dependence of the f occupancy which value is crucial for the interpretation of various physical properties. However, the validity of the SIAM for heavy fermions has been questioned [3] based on the inconsistency of experimental data obtained by electron spectroscopies. In particular, the existence or lack of the Kondo resonance in valence-band photoemission spectra of heavy fermion materials is heavily debated. A large surface contribution to the spectra often complicates the analysis of the bulk component. In this case, the bulk sensitivity and element-specific nature of resonant soft-x-ray scattering spectroscopy is particularly useful.

This abstract presents soft-x-ray scattering data recorded at different excitation energies across the Ce 4d absorption edges of CeB_6, CeAl, γ-Ce, and α-Ce.

EXPERIMENTAL DETAILS

A single crystal of CeB_6 was grown by the floating-zone method [4]. The CeAl sample was a polycrystal prepared by induction melting from stoichiometric amounts and checked by x-ray diffraction and microprobe analysis. The Ce-metal sample was a 1.0-mm thick film of the 99.9 % purity which was supplied by Alpha Aesar Co. Fresh surfaces of the samples were obtained by scraping with a diamond file. To study the γ- and α-phases of Ce the measurements were carried out at 300 K and 40 K, respectively, using a closed-cycle cryogenic system.

The experiments were performed at beamline 7.0 of the Advanced Light Source, Lawrence Berkeley National Laboratory with a spherical grating monochromator [5]. The scattering spectra of Ce-based materials were recorded using a grazing-incidence grating spectrometer [6] with a two-dimensional detector. The spectrometer resolution was set to about 140 meV. The incidence angle of the photon beam was about 20˚ from the sample surface and the spectrometer was placed in the

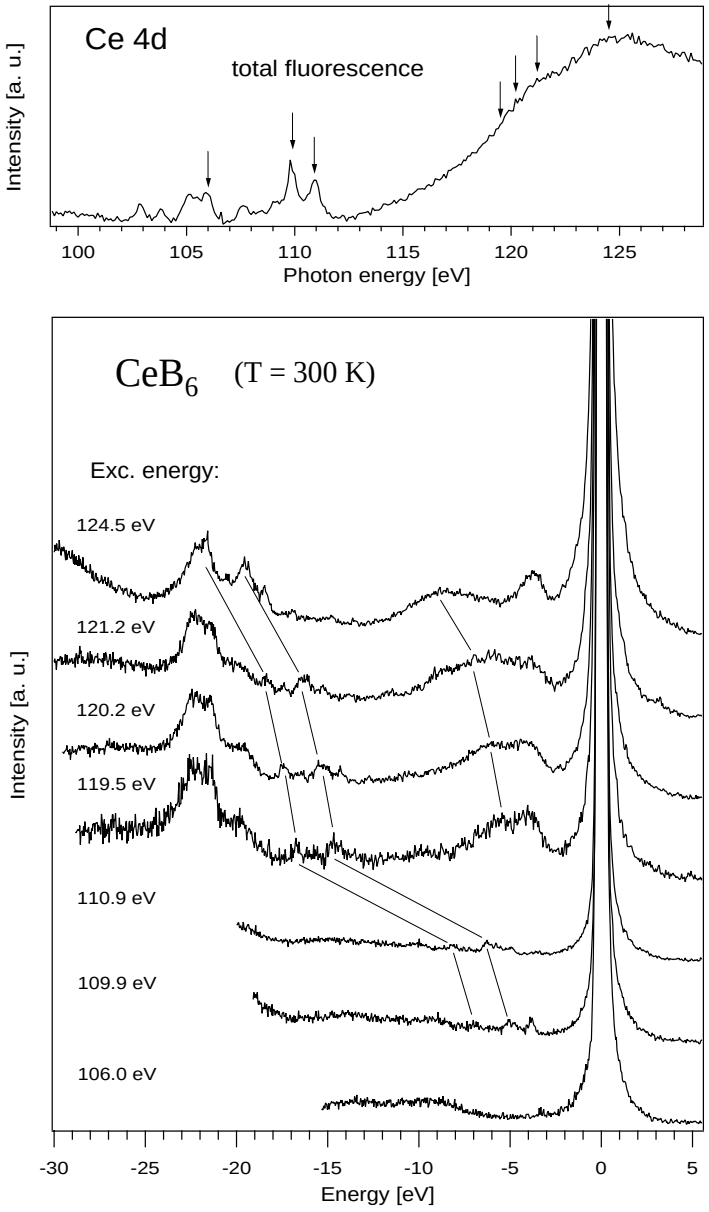

Figure 1. Resonant inelastic soft-x-ray scattering spectra of CeB_6. The elastic peak is set at 0 eV. The excitation energies used to obtain these spectra are indicated by arrows on the total fluorescence spectrum at the Ce 4d edge shown in the top panel.

horizontal plane at an angle of 90˚ with respect to the incidence beam. To determine the excitation energies, total fluorescence yield spectra of the Ce 4d edge were recorded in the same experimental geometry using the spectrometer detector. During the absorption and scattering measurements, the resolution of the monochromator was set to about 120 meV.

RESULTS AND DISCUSSION

Fig. 1 shows resonant soft-x-ray scattering spectra of CeB_6 which reveal pronounced inelastic scattering structures within 30 eV below the elastic peak when the excitation energy is close to the main Ce 4d absorption edge. Due to dipole selection rules, the structures with low energy losses represent transitions to the final states of 4f symmetry via creation-annihilation of a 4d core hole (the scattering cross-section for the 6p states is much lower). Lines at energy losses of about 19.5 and 22 eV correspond to transitions to the final states of 5p symmetry. The CeB_6 spectra also show non-resonant x-ray fluorescence structures which mainly reflect the 4f–4d radiative decay. These structures move to the high energy loss side with increasing excitation energies. The movement of the structures in different spectra is indicated with lines in Fig. 1.

The lowest inelastic scattering structure which is clearly resolved has an energy loss of about 3.7 eV. It gains intensity as the excitation energy is tuned towards the main Ce 4d absorption edge. In Fig. 2 the 4-eV-energy-loss structure is also observed in the resonant soft-x-ray scattering spectra of α-Ce. Tuning the excitation energy across the Ce 4d edge gives rise to a distinct resonance of this structure. It's intensity reaches a maximum at an excitation energy of about 124.5 eV but decreases at 133.3 eV. A similar structure was previously observed in low-energy electron-energy-loss spectra of Ce [7,8] and was assigned to inter-band f–d transitions. Here, the selection rules

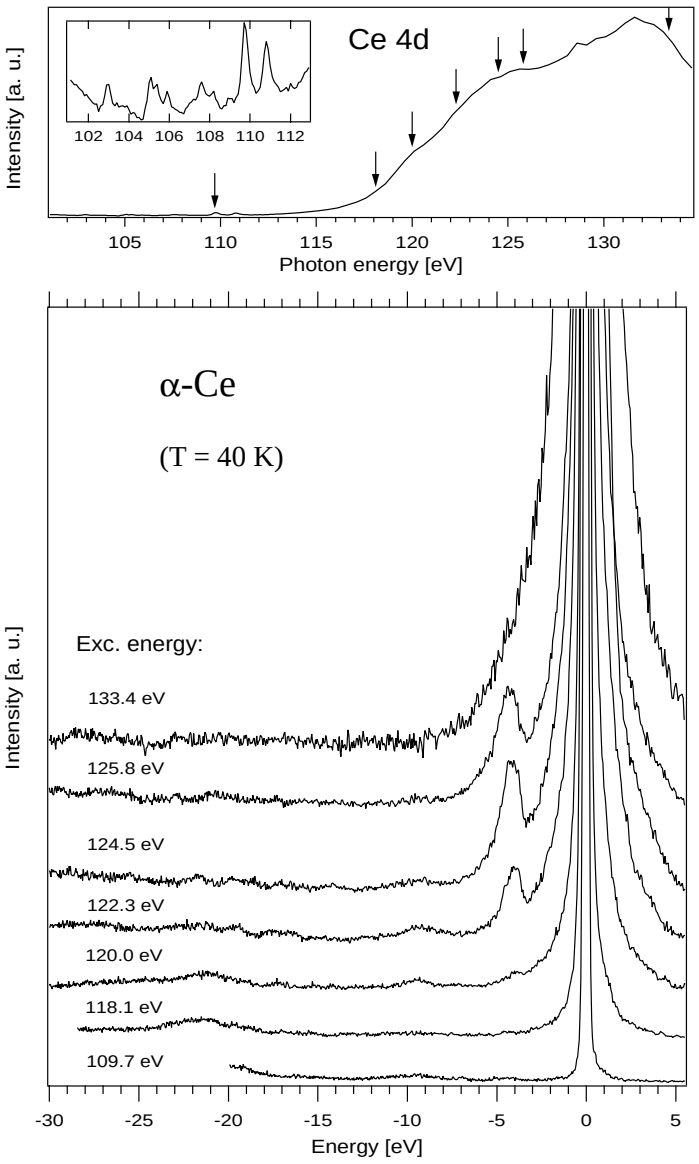

Figure 2. Resonant inelastic soft-x-ray scattering spectra of α-Ce. The excitation energies used to obtain these spectra are indicated by arrows on the total fluorescence spectrum at the Ce 4d edge shown in the top panel.

dictate that the 4-eV structure must have 4f character. A comparison of inelastic scattering spectra of different systems (Fig. 3) recorded at the same excitation energy shows that the energy loss of this structure somewhat increases on going from systems with weakly hybridized 4f states to those with strongly hybridized 4f states.

The 4f nature of the 4-eV-energy-loss inelastic scattering structure, its resonant behavior and dependence on the hybridization strength strongly suggest that the structure corresponds to charge-transfer excitations resulting from configurational mixing in the ground and intermediate states of a coherent second-order optical process. For the ground state described as a linear combination of f^1, f^0, and f^2 configurations, the 4-eV structure is expected to have mainly f^0 character as the lowest observable excitation peak (excited states of the f^1 configuration separated by the Kondo energy $k_B T_K$ from the singlet ground state can not be resolved with the experimental resolution used).

In the present case, the derived energy of 4 eV required for charge-transfer excitations to the f^0 state is higher than the binding energy of the f^0 peak (2.5 eV) in valence-band photoemission spectra [2]. The difference between the two techniques can be a result of probing systems with a different number of electrons. The x-ray scattering process is charge neutral while photoemission spectroscopy probes the *N-1* particle system. The difference is not surprising when considering strong configurational dependence of the SIAM parameters [9]. The reduction in the value of the hybridization matrix element V_{km} between f and conduction states with respect to that derived from first principle calculations or from the analysis of low-energy thermodynamic properties is required to describe photoemission data. As follows from the present interpretation of the scattering spectra, both the bare energy ε_f of f states and V_{km} which contribute to the energy separation between f^1 and f^0 configurations can be larger than those obtained from fitting photoemission data.

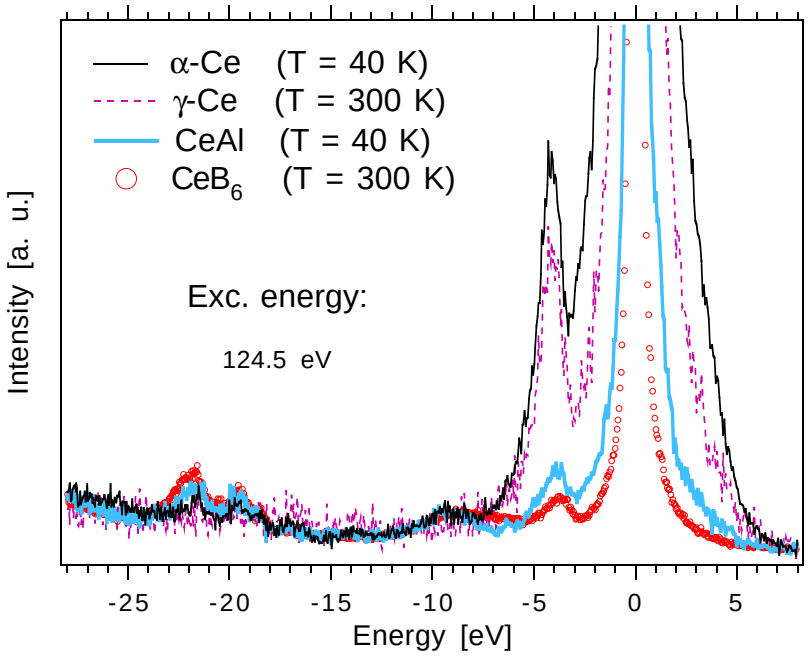

Figure 3. A set of inelastic soft-x-ray scattering spectra of several Ce-based systems recorded at the excitation energy of 124.5 eV. The spectra were normalized to the same intensity of both non-resonant fluorescence structures and background.

Finally, the elastic peak which corresponds to transitions back to the ground state shows an intriguing dependence on the Kondo temperature of the studied systems. It's intensity scales as α-Ce (1.0); γ-Ce (0.4); CeAl (0.19); CeB_6 (0.06) which is consistent with a Kondo-scale behavior (note, measurements on CeAl and CeB_6 were done at different temperatures). However, unknown contributions from diffuse scattering due to surface roughness of the samples and self-absorption effects introduce a very large uncertainty. Further measurements using smooth surfaces and experimental conditions reducing the diffuse scattering contribution are necessary to firmly establish this behavior.

REFERENCES

1. S. M. Butorin et al., Phys. Rev. Lett. **77**, 574 (1996); S. M. Butorin et al., J. Alloys Compounds **225**, 230 (1995); S. M. Butorin et al., J. Phys. Condens. Matter. **9**, 8155 (1997).
2. e.g. D. Malterre et al., Adv. Phys. **45**, 299 (1996).
3. e.g. J. J. Joyce et al., Phys. Rev. Lett. **68**, 236 (1992).
4. N. Sato et al., J. Phys. Soc. Jpn. **53**, 3967 (1984).
5. T. Warwick et al., Rev. Sci. Instrum. **66**, 2037 (1995).
6. J. Nordgren et al., Rev. Sci. Instrum. **60**, 1690 (1989).
7. J. Bloch et al., Phys. Rev. B **30,** 2462 (1984).
8. E. P. Netzer et al., Surf. Sci. **152-153**, 757 (1985).
9. O. Gunnarsson and O. Jensen, Phys. Rev. B **38**, 3568 (1988).

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Principal investigator: E. Joseph Nordgren, Physics Department of Uppsala University, Sweden. E-mail: joseph.@fysik.uu.se